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NATIONAL ADVISORY COMMITTEE FOR AERONAUTICS

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HIGH-TEMPERATURE PROTECTION OF A TITANIUM-CARBIDE
CERAMAL WITH A CERAMIC-METAL COATING HAVING
A HIGH CHROMIUM CONTENT

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National Bureau of Standards



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SUMMARY

In an effort to retard oxidation at high temperatures of a ceramal containing 80 percent titanium carbide and 20 percent cobalt, a protective ceramic-metal coating was developed. This coating was designated A-479M and contained 80 percent by weight of chromium powder and 20 percent by weight of an alkali-free frit (glass). It was prepared as a water suspension (slip), containing the powdered frit and powdered metal with clay as the floating agent. This suspension was applied to the ceramal by either dipping or spraying. After drying, the coating was bonded to the ceramal by firing at 2200° F for 10 minutes in a purified hydrogen atmosphere.

The fired coating was hard, smooth, and adherent. Microscopic examination of sections cut at right angles to the interface showed the presence of a chromium-rich bond layer with numerous metal particles of the coating welded to the layer and to each other.

Oxidation tests in air for 200 hours at 1800° F made with both coated and uncoated specimens showed that the effective thickness of an uncoated specimen decreased 0.0365 inch because of formation of oxide, while the coated specimen showed no significant decrease. A thermal shock test made after the 200-hour oxidation test indicated that the coating was equally as resistant as the ceramal to thermal shock failure.

A deformation test, made on a bar-type specimen pressed from the coating material, showed that a deformation of 1.3 percent was possible without cracking at a temperature of 1500° F, thus indicating that the coating could be expected to creep with a ceramal turbine blade when operated at temperatures of 1500° F or above.

The various laboratory tests indicated that the A-479M coating would greatly prolong the life of an 80-percent titanium-carbide and 20-percent cobalt ceramal turbine blade at 1800° F, under operating conditions sufficiently severe to accelerate failure of the uncoated blade by formation of oxide.

INTRODUCTION

High-temperature alloys in current use for gas-turbine blades give reasonably good service at a gas inlet temperature that does not exceed 1650° F except for short periods, for example, during starting. Under these conditions (1650° F gas temperature), the blade temperature is in the range of 1500° to 1550° F. Any substantial increase of blade temperature above this range results in a reduction in the life of the blade. Because of this temperature restriction of current blade alloys, the increase in thermal efficiency of the gas turbine with increasing gas temperature cannot be fully utilized, and for this reason there is a concerted effort to develop materials that have improved physical properties at the elevated temperatures.

One such material is a cobalt-bonded, titanium-carbide ceramal¹. This is a proprietary product manufactured by Kennametal, Inc. and identified as K-138. The tensile strength of the K-138 composition at 1800° F is reported to be 31,800 psi (reference 1). Accelerated blade tests made with blades of the supercharger type have shown this material to have promise for high-temperature operation (reference 1).

A potential weakness of the K-138 composition is a progressive oxide formation that occurs when the material is heated for prolonged periods. Bobrowsky (reference 2), in discussing ceramals of this type, states that the oxidation rates at moderate operating temperatures are not excessive but those at inlet gas temperatures of 2100° to 2200° F (approximately 2000° F blade temperature) are so high that the life of a turbine blade would probably be limited by oxidation to about 10 hours. Better oxidation resistance is obviously desirable and one possible method of retarding the oxidation is by the application of a protective coating.

The present report describes the development of such a coating at the National Bureau of Standards under the sponsorship and with the financial assistance of the National Advisory Committee for Aeronautics.

¹A ceramal may be defined as any sintered or hot-pressed material consisting of a combination of ceramic and metallic ingredients. All carbides are considered as ceramic materials.

MATERIALS

The ceramal specimens used were prepared by Kennametal, Inc., Latrobe, Pennsylvania. The composition of the K-138 ceramal, furnished by the manufacturer, is 80 percent by weight of titanium carbide bonded with 20 percent by weight of cobalt. The specimens were $2\frac{1}{2}$ inches by $\frac{3}{4}$ inch by $\frac{1}{8}$ inch with a $\frac{1}{8}$ -inch-diameter hole near one end. All corners and edges were rounded but the flat surfaces were not finish-ground.

The frit used in the preparation of practically all coatings was an alkali-free composition with the assigned number 331. The composition of this frit is shown in table 1. It was selected because previous tests had indicated that its ingredients were noncorrosive toward the more common heat-resistant alloys at temperatures above 1500° F. (reference 3) and for this reason it was believed that it might also be nonreactive toward the cobalt-bearing K-138 and the chromium powder. The chromium powder was procured from Charles Hardy, Inc., New York, New York. It was prepared electrolytically. The spectrochemical analysis and particle size distribution are given in table 2. The clay was a commercial grade of Florida kaolin.

The ceramic seal coats used were prepared by the National Bureau of Standards and are designated as A-406c and L-7c.

DEVELOPMENT OF COATING

Exploratory applications to the K-138 ceramal were made using ceramic coatings that had previously been applied to heat-resistant alloys. These ceramic coatings retarded the rate of oxide penetration of the K-138 but were somewhat lacking in adherence. They also showed strong tendencies toward blistering after prolonged heating, thus giving a finish with an undesirable roughness.

In an effort to overcome these weaknesses in the ceramic coating, trial mixtures were prepared in which chromium powder formed a substantial part of the coating. Promising results were obtained and further trials were indicated. Chromium powder was selected for the metallic admixture because of: (a) Its high resistance to oxidation, (b) its thermal expansion which closely matches that of the K-138 and, (c) its inherent hardness and resistance to abrasion. The frit or glass phase was considered desirable to give a coating that was less permeable to air and also to retard oxidation of the chromium particles.

Preparation and Study of Compacts of Varying Chromium-Frit Ratios

In order to determine the effect of the frit in retarding the oxidation of the chromium powder, a number of compacts of varying compositions were prepared. In preparing these compacts, each of the mixtures listed in table 3 was ball-milled for 10 minutes. After adjusting the resulting water suspension to give a consistency suitable for applying to the K-138 specimens by dipping, the suspension, or slip, was cast on filter paper laid on a flat plaster surface. The resulting dried slabs were presintered for 20 minutes at 1500° F in argon, after which eight specimens 2 inches by 1/2 inch by 3/16 inch were cut from each slab. After marking for identification, a hole of 1/8-inch diameter was drilled near the top of each specimen.

Duplicate specimens of each composition were sintered in argon for 30 minutes at 1800° F, another set at 2000° F, and a third set at 2200° F. The appearance of these compacts after sintering is shown in figure 1. Some of the compacts, representing compositions and sintering conditions that resulted in bloating, were rejected without further test and the remainder were heated in air for 140 hours at 1650° F, the gain in weight being determined at 20-hour intervals.

Figure 2, which is a plot of data obtained after 100 hours of heating, shows the effect of both sintering temperature and frit content on the percentage of the total chromium oxidized. The percentage chromium oxidized was computed from the average gain in weight of duplicate compacts. In these computations it was assumed that all of the weight gain was represented by the reaction $4\text{Cr} + 3\text{O}_2 = 2\text{Cr}_2\text{O}_3$. This assumption was based upon the fact that all of the compacts after heating in air had the characteristic green color of chromic oxide Cr_2O_3 .

Preparation of Coating and Test Specimens

From the data of figure 2, a composition consisting of 80 percent by weight of chromium and 20 percent by weight of frit 331, sintered at 2200° F, was selected for coating trials with the K-138 ceramal.

The following coating, designated A-479M, was prepared to represent this composition:

Electrolytic chromium powder (-100 mesh), grams	800
Frit 331 (-100 mesh), grams	200
Florida kaolin, grams	50
Sodium pyrophosphate, $\text{Na}_4\text{P}_2\text{O}_7$ (saturated), ml	7
Sodium nitrite, NaNO_2 (saturated), ml	1.5

The mixture was milled for $2\frac{1}{2}$ hours in a 1-gallon ball mill. The linear thermal expansion (from 20° to 600° C) after sintering at 2200° F in hydrogen for 10 minutes was 9.6×10^{-6} per $^{\circ}$ C.

This coating was applied to sandblasted K-138 specimens by dipping. After drying, the coating was fired by suspending the specimens in a small, fused-silica, gas-fired tube furnace and heating them to 2200° F for 10 minutes in an atmosphere of purified hydrogen. The hydrogen was purified by first removing the oxygen with a palladium catalyzer and then drying the gas by first passing through lump calcium chloride and then through magnesium perchlorate. Hydrogen was used for the firing operation rather than argon because preliminary experiments had indicated that the hydrogen atmosphere gave a somewhat more resistant coating. Also, hydrogen was selected because, in comparison with argon, it is cheaper and more easily purified.

Some of the A-479M coated specimens were given ceramic seal coats of A-406c or L-7c. Other specimens were coated with the all-ceramic coating, A-406c. The compositions of these two coatings are given in tables 4 and 5. (The composition of frit 228 used in coating L-7c is given in table 6.)

TEST PROCEDURE AND RESULTS

Oxidation Tests

Oxidation tests on both the coated and uncoated specimens were made in air at 1800° F, the gain in weight being determined at intervals up to 200 hours. The loss in thickness after 200 hours was determined for both the uncoated and the coated specimens. The thickness of the K-138 specimens was measured with a micrometer before the coating was applied and again after removal of the coating layer by sandblast. Similarly, measurements were made after removal of the oxide layer on the uncoated specimens using the same procedure.

In the sandblast operation, low-pressure air was used in conjunction with 60 mesh glass sand. The point where coating or oxide removal was complete was indicated by a sharp change in appearance. The loss in thickness corresponding to shorter heating periods was computed from the the gain-in-weight data. In this computation, it was assumed that the ratio of reduction of thickness to gain in weight was constant and independent of the duration of heating.

Table 7 shows the effectiveness of the various coatings in preventing loss of thickness of K-138. Figure 3 provides a graphic comparison of the loss in thickness of the various coated and uncoated specimens.

As indicated in table 7, the surface appearance of the K-138 specimens coated with A-479M was excellent after 200 hours' heating at 1800° F. The coating retained its original smoothness and the only major change was one of color. The coating surface changed from an initial metallic appearance to the characteristic green of chromic oxide Cr_2O_3 .

Thermal Shock Tests

In previous work with ceramic coatings, it was found that prolonged heat treatment reduced the thermal shock resistance of the coating. Consequently, a thermal shock test of the A-479M coating on K-138 was made after the 200 hours' heating in air at 1800° F rather than before this treatment. Also, owing to the suspected good resistance of the coating to thermal shock, the test was made more severe than would be encountered in service in order to reduce the testing time to a minimum.

The test selected was carried out as follows: The specimens were heated for 5 minutes at a temperature of 1000° F, then withdrawn quickly from the furnace, and the lower ends submerged to a depth of 1 inch in water at room temperature. After 5 minutes in the water, the specimens were examined and, if no failure had occurred, they were reinserted into the furnace at a 100° F higher temperature and the cycle was repeated. This procedure was continued until failure occurred or until the specimens had been quenched from 2200° F without failure.

Table 8 gives the results of these thermal shock tests. No failures occurred on the first quench from 1000° F, but failures of the seal coats took place on the next cycle (1100° F). The adherence of the oxide layer on the uncoated specimens was surprisingly good, the layer remaining on the specimen until the 1200° F quench.

All of the specimens having A-479M coatings (without seal coats) withstood thermal shocks up to the quench from 1800° F, when a fine crack appeared about 3/4 inch from the lower end. Subsequent examination indicated that this crack originated in the K-138 itself rather than in the coating.

Microstructure

Figure 4 shows the microstructure of unetched and etched sections through the interface between the A-479M coating and the K-138 ceramal taken at magnifications of 1750X and 800X, respectively. These pictures show clearly the presence of a "bond layer." The presence of this layer was noted on all specimens examined in which coating A-479M had been applied to K-138. When the A-479M coating was stripped from the specimens by sandblast, this layer had a bright and silverlike appearance in contrast with the rather dull appearance of the K-138.

The average layer thickness when the A-479M was fired 10 minutes at 2200° F was about 0.00025 inch, as measured by microscopic methods. When fired for 1 hour at the same temperature it increased to 0.00043 inch, while firing for 15 minutes at 2350° F increased the thickness to 0.00037 inch.

An X-ray diffraction analysis of the layer did not permit a positive identification². It did show, however, that the layer was neither chromium nor cobalt as such. Two of the three known chromium carbides were also eliminated by this means. There was some agreement with published data for chromium carbide Cr_7C_3 but the agreement was not sufficient to allow a positive identification. Spectrochemical tests³ showed only that there was a higher concentration of chromium at the shiny layer than there was immediately below the layer and also that the concentration of chromium in the layer appeared to be comparable with the concentration of chromium in the coating.

A change in characteristics of the ceramal as the bond layer is approached is indicated in figure 4, especially in the etched section taken at a magnification of 800X. The significance of this change is not as yet known, but figure 5 shows that it did not occur when an uncoated specimen was given the same firing treatment as the specimen shown in figure 4 (in hydrogen for 10 min at 2200° F), nor did it occur when a coating of frit 331 with no chromium admixture was applied and fired under the same conditions.

Two specimens were sandblasted to remove coating A-479M down to the shiny bond layer over two-thirds of their areas. The bond layer was removed from one-half of these exposed areas, giving specimens one-third uncoated, one-third fully coated, and one-third with the bond layer only. These specimens were then heated in air at 1800° F. No significant protection was provided by the bond layer, that area of each specimen oxidizing equally as fast as the area from which the bond layer had been removed.

Figure 6 shows sections across the coating-ceramal interface of specimens that had been heated for 200 hours in air at 1800° F. Only minor changes in microstructure are apparent in figure 6(a), and it appears that the coating was still giving good protection to the ceramal. In figure 6(b) an area is shown where an apparent localized oxidation of the K-138 ceramal, about 0.001 inch wide and 0.001 inch deep, has occurred. Numerous areas of this type were noted on A-479M coated specimens after the 200 hours' heating in air at 1800° F. It is possible that these

²Analysis made by Mr. H. E. Swanson of the Constitution and Microstructure Laboratory at NBS.

³Tests made by Spectrochemistry Section of NBS under the supervision of Mr. B. F. Scribner.

areas represent the early stages of a deterioration that would ultimately result in failure. The apparent oxide penetration in figure 6 was, however, only about one-eighteenth as deep as the oxide penetration on the uncoated specimen that had been subjected to the same heat treatment. The application of seal coat A-406c did not eliminate these areas of localized oxidation but greatly reduced their number. Seal coat L-7c apparently eliminated this type of oxidation but caused or permitted an effect that changed the appearance of the bond layer and allowed some slight surface oxidation (or other corrosion) in areas where there was little or no bond layer.

Examination of sections before and after the 10-minute heating at 2200° F in hydrogen indicated no change in structure of the K-138 material resulting from the heat treatment involved in firing the coating on the specimen.

Deformation Test of Chromium-Frit Coating

Because of the large chromium content in the A-479M type of coating, it was desirable to determine whether there would be sufficient flow at elevated temperatures to allow the coating to creep with the underlying base material. Unless the coating would creep with the base material as much as is tolerated in service, cracking of the coating might result with corresponding loss of effectiveness.

Figure 7 shows the results of a deformation test made with a bar-type specimen formed from coating A-483M⁴. The lower specimen in this figure was tested, after firing, with quarter-point loading at 2000 psi for 18 hours in air at 1500° F. The measured extension on the tension side was 1.3 percent and there was no evidence of cracking.

DISCUSSION

One of the more interesting findings of the study of chromium-frit compacts was the effect of the frit in retarding the oxidation of the chromium powder. Figure 2 shows, for example, that after sintering at 2200° F the percentage of the original chromium oxidized after 100 hours' heating in air at 1650° F is only about one-tenth as much when 20 percent of frit 331 is present as when no frit is present. The glassy phase (frit) apparently inhibits oxidation by flowing around the chromium grains, thus sealing the metal particles from contact with air. This mechanism could not occur if, instead of the frit, an admixture of refractory oxide were used.

⁴The A-483M coating is similar to A-479M except that it contains -200 mesh chromium rather than -100 mesh chromium.

The 1650° F temperature selected for the oxidation test of the compacts in air is low compared with the expected operating temperature of the K-138. However, the same trends would be expected at 1800° and 2000° F as at 1650° F and hence the data are of value as a basis of coating selection.

The test temperature used for the long-time heating of the coated K-138 specimens was 1800° F. At this temperature, oxidation of the uncoated K-138 is appreciable. Bobrowsky (reference 2) reports an "oxidation penetration" of 0.011 inch during 100 hours at 1800° F in air, which compares with that of 0.012 inch obtained from figure 3 by dividing the total loss in thickness of the uncoated K-138 at 100 hours by 2 to obtain the oxide penetration on one surface.

- Figure 3 shows that by applying a 0.009-inch layer of coating A-479M the loss in thickness of a K-138 specimen after 200 hours' heating in air at 1800° F can be reduced to 0.0003 inch as against 0.0365 inch for an uncoated specimen. These values are subject to some error owing to the sandblasting technique that was used for removal of both the coating and the oxide scale prior to the final measurement of thickness. This error is believed to be in the fourth decimal place.

Figure 6 indicates that after the 200 hours' heating at 1800° F perfect protection of the K-138 was not achieved by the A-479M coating. A number of localized areas of apparent oxidation, such as that shown in figure 6(b), were noted in the microscopic examination and until such areas can be eliminated the ultimate protection cannot be achieved. The application of a suitable seal coat somewhat different from either L-7c or A-406c is believed to represent one possibility of reaching this objective.

The thermal shock resistance of the A-479M coating appears to be excellent. The test described is many times more severe than would be expected in service and in this test the coating was equally as resistant as the K-138 specimen. Hoffman, Ault, and Gangler (reference 1) described a test involving air-quenching from successively higher temperatures and reported that the ceramal containing 80 percent titanium carbide and 20 percent cobalt withstood the full treatment without failure, including 25 cycles of quenching from the maximum temperature of 2400° F.

No information is available regarding the creep properties of the K-138 ceramal at elevated temperatures. However, some creep would be expected and, for the A-479M coating to maintain its effectiveness, the coating would need to deform with the ceramal. That the A-479M coating is capable of deformation without cracking at temperatures as low as 1500° F is demonstrated in figure 7. At higher temperatures greater deformability would be expected. This evidence thus indicates that the A-479M coating, when applied to a turbine blade and operated in a turbine,

could be expected to creep with the blade without loss of its protective properties.

The mechanism through which the A-479M coating becomes bonded to the K-138 titanium-carbide and cobalt composition is not completely understood. The presence of the chromium-rich layer, however, is believed to aid in the adherence. Microscopic examination reveals that the particles of chromium present in the coating have become welded to the layer at numerous points, as well as to each other, and that the layer in turn is firmly attached to the K-138 composition.

It is believed that the bond layer shown in figures 4 to 6 is rich in chromium carbide. This belief is strengthened by the X-ray analysis and also by the behavior of the coating when applied to other materials. It was found, for example, that the A-479M had very poor adherence when fired at 2200° F in hydrogen on such alloys as S-816, H.S. 21 (a cobalt-chromium alloy), and Hastelloy B, and yet adhered very well to recrystallized silicon carbide and to zirconium carbide when applied under the same conditions. Because of these results, it is thought that the adherence is at least in part dependent on the formation of chromium carbide at the interface. A possible contradiction to this theory, however, is that the coating does not adhere well to graphite.

All of the test data so far obtained indicate that a prolonged life could be expected with the A-479M coating applied to a K-138 turbine blade when operated under oxidizing conditions. Oxide penetration at an operating temperature of 1800° F, which amounts to as much as 0.012 inch in 100 hours in an air atmosphere, would be greatly retarded. The laboratory study indicates that both the adherence and the thermal shock resistance of the coating should be adequate for turbine blades.

Application of the coating to a turbine blade should not present any special difficulties. The application thickness of about 0.008 inch is not excessive and the coating could be applied by either dipping or spraying, depending on the type of blade being coated. It has been found that a good atmosphere is essential during firing, but it is believed that commercial furnaces suitable for the purpose could be made available. There is apparently no important change in structure of the K-138 from the 2200° F firing treatment.

CONCLUSION

The present investigation has demonstrated the feasibility of protecting a cobalt-bonded titanium-carbide (Kennametal K-138) ceramal

against oxidation by the application of a ceramic-metal coating having a high content of chromium powder. Laboratory tests have indicated that the new coating has adequate adherence and thermal shock resistance and also that it would be expected to creep at a temperature as low as 1500° F.

At a blade temperature of 1800° F the A-479M coating would probably greatly prolong the life of a K-138 turbine blade under operating conditions sufficiently severe to accelerate failure of the uncoated blade by oxidation.

National Bureau of Standards

Washington, D. C., June 27, 1949

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2. Bobrowsky, A. R.: The Applicability of Ceramics and Ceramals as Turbine-Blade Materials for the Newer Aircraft Power Plants. Trans. A.S.M.E., vol. 71, no. 6, Aug. 1949, pp. 621-629.
3. Moore D. G., Richmond, J. C., and Harrison, W. N.: High-Temperature Attack of Various Compounds on Four Heat-Resisting Alloys. NACA TN 1731, 1948.

TABLE 1.- BATCH COMPOSITION AND COMPUTED OXIDE

COMPOSITION OF FRIT 331

[Maximum smelting temperature, 2425° F;
smelting time, $2\frac{1}{2}$ to 3 hr]

(a) Raw batch composition.

Constituent	Parts by weight
Flint (silicon dioxide)	38.00
Barium carbonate	56.63
Boric acid	11.50
Calcium carbonate	7.14
Beryllium oxide	2.50
Zinc oxide	5.00
	<u>120.77</u>

(b) Computed oxide composition.

Oxide	Percent by weight
SiO ₂	38.0
B ₂ O ₃	6.5
BaO	44.0
CaO	4.0
ZnO	5.0
BeO	2.5
	<u>100.0</u>



TABLE 2.- SPECTROCHEMICAL ANALYSIS AND PARTICLE SIZE
OF -100 MESH ELECTROLYTIC CHROMIUM POWDER
USED IN CERAMIC-METAL COATING A-479M

(a) Spectrochemical analysis.¹

Indicated strength of elements tested			
Trace (<0.01 percent)	Very weak (<0.01 percent)	Weak (0.01 to 1 percent)	Very strong (>1 percent)
Ag Al Cu Mg Ni Pb Sn Ti	Ca Co Mn Mo	Fe Si	Cr

(b) Particle size.²

Method of determination	Particle size
Microprojection	Largest diameter, 250 microns Smallest diameter, 1-2 microns Apparent average diameter, 110-120 microns
Air permeability (Fisher Sub-Sieve Sizer)	Average diameter, 37.0 microns
Wagner Turbidimeter	14 percent of sample less than 60 microns Specific surface area, 82.3 cm ² /gram

¹Analysis by Spectrochemistry Section at NBS.

²Analysis made under direction of Mr. R. L. Blaine of the Fineness Laboratory at NBS.



TABLE 3.- BATCH COMPOSITIONS USED FOR PREPARATION
OF CERAMIC-METAL COMPACTS

Batch	Parts by weight of -		
	Frit 331 ^a	-100 Mesh chromium powder ^b	Florida kaolin
A	0	100	5
B	5	95	5
C	10	90	5
D	15	85	5
E	20	80	5
F	25	75	5
H	30	70	5

^aSee table 1 for frit composition.

^bElectrolytic grade.

TABLE 4.- MILL FORMULA FOR CERAMIC COATING A-406c

[Milling fineness, trace on 200 mesh sieve from 50-ml sample of coating slip; milling time, 6 hr in 1-gal jar mill with 1040-gram charge of dry material and 420 ml of water; firing temperature, 1850° F]

Constituent	Parts by weight
Frit 331 ^a (through 6 mesh)	75
Wollastonite (calcium silicate)	20
Chromic oxide	5
Florida kaolin	4
Sodium nitrite	.05
Water	42

^aSee table 1 for composition.



TABLE 5.- MILL FORMULA FOR CERAMIC COATING L-7c

[Milling time, 17 hr in 1-gal ball mill with 1060-gram charge of dry material and 500 ml of water; milling fineness, 100 percent through 200 mesh sieve; firing temperature, 1650° F; fired thickness, 0.001 to 0.002 in.]

Constituent	Parts by weight
Frit 228 ^a (through 6 mesh)	70
Chromic oxide (commercial grade)	30
Enameler's clay	6
Water	50

^aSee table 6 for composition.



TABLE 6.- BATCH COMPOSITION AND COMPUTED OXIDE

COMPOSITION OF FRIT 228

[Maximum smelting temperature, 2400° F;
smelting time, approximately $1\frac{1}{2}$ hr]

(a) Raw batch composition.

Constituent	Parts by weight
Potash feldspar	28.31
Borax	24.59
Flint	33.78
Titanium dioxide	5.00
Soda ash	15.21
Potassium nitrate	4.47
Litharge	5.00
Fluorspar	2.67
Cobalt oxide	1.50
Nickel oxide	.50
Manganese dioxide	.35
	<u>121.38</u>

(b) Computed oxide composition.

Oxide	Percent by weight
SiO ₂	52.4
TiO ₂	5.0
Al ₂ O ₃	5.5
B ₂ O ₃	9.0
K ₂ O	4.3
Na ₂ O	13.8
CaF ₂	2.7
PbO	5.0
CoO	1.5
NiO	.5
MnO ₂	.3
	<u>100.0</u>



TABLE 7.- DECREASE IN THICKNESS OF KENNAMETAL K-138 AND
APPEARANCE OF COATED AND UNCOATED SPECIMENS AFTER
200 HOURS' HEATING IN AIR AT 1800° F

Specimen (1)	Coating	Coating thickness (in.)	Condition after 200-hr heating in air at 1800° F	
			Loss in thickness of K-138 (in.) (2)	Surface appearance
10	A-479M (one coat)	0.0062	0.0009	Smooth surface, dark green color, some oxidation of K-138 at support hole
12	A-479M (two coats)	0.0087	0.0003	Smooth surface, dark green color, no evidence of oxidation of K-138, slight chipping of second coat at edges
15	A-406c over A-479M	0.0065	0.0002	Rough scaly surface, light green color, slight evidence of oxidation of K-138 at support holes
16	L-7c over A-479M	0.0064	0.0008	Semismooth surface, dark green on flat surfaces, almost black on edges, very slight oxidation of K-138 on bottom edge, no chipping
18	A-406c (one coat)	0.0019	0.0307	Moderately rough surface, steel gray color, cracks in coating, slight chipping at edges, evidence of oxidation beneath surface
19	Uncoated	0	0.0365	Moderately rough surface, dark gray color, some chipping and cracking of oxide layer, evidence of severe oxidation

¹Duplicate specimens used for studies of microstructure.

²Determined after removal of oxide or coating layer by light sandblast.

TABLE 8.- RESULTS OF THERMAL SHOCK TESTS WITH COATED AND UNCOATED KENNAMETAL K-138

SPECIMENS THAT WERE PREVIOUSLY HEATED FOR 200 HOURS IN AIR AT 1800° F

Specimen	Coating	Effect after quenching in water from temperatures (°F) of - (a)												
		1000	1100	1200	1300	1400	1500	1600	1700	1800 (b)	1900	2000	2100	2200
9	A-479M (two coats)	N	N	N	N	N	N	N	N	N	N	N	N	N
10	A-479M (one coat)	N	N	N	N	N	N	N	N	N	N	N	NC	NC
12	A-479M (two coats)	N	N	N	N	N	N	N	N	N	N	N	NC	NC
13	A-479M (two coats)	N	N	N	N	N	N	N	N	N	N	N	NC	NC
15	A-406c on A-479M	N	N	N	N	N	N	N	N	N	N	N	NC	NC
16	L-7c on A-479M	N	N	N	N	N	N	N	N	N	N	N	NC	NC
18	A-406c (one coat)	N	N	N	N	N	N	N	N	N	N	N	NC	NC
21	Uncoated	N	N	N	N	N	N	N	N	N	N	N	NC	NC

^aLetter symbols refer to degree of effect after quenching. N, no flaking; L, slight flaking; M, moderate flaking; S, severe flaking; VS, very severe flaking; NC, no change.

^bOne fine crack visible in coating surface which was later determined to be cracking of K-138.

^cNo previous heat treatment.

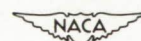
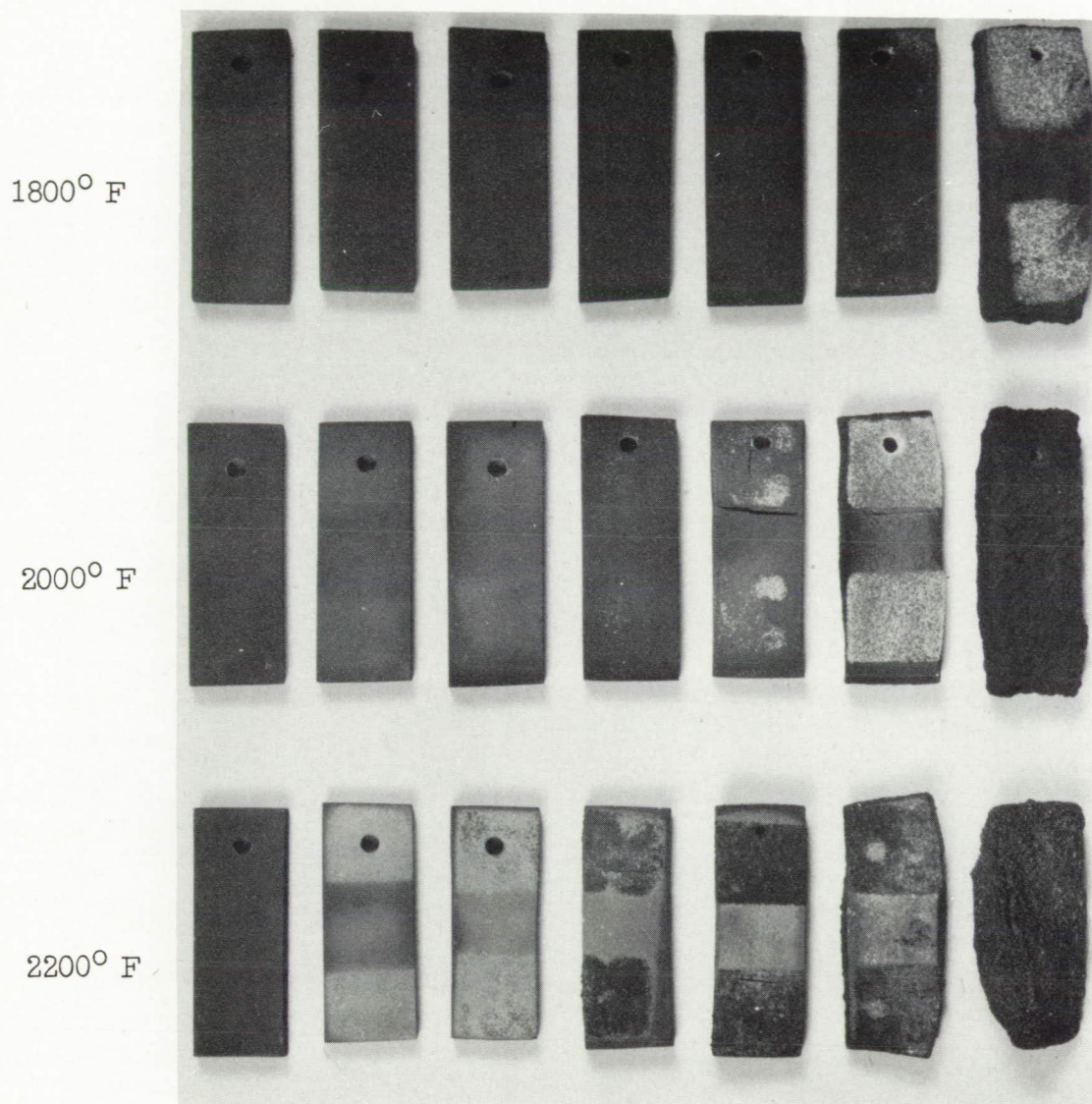
^dCoating separated from K-138.

^eFailed during heating cycle.



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Frit	0	10	20	30	40	50	60
Cr powder	100	90	80	70	60	50	40

Figure 1.- Compacts with various proportions of chromium powder and frit 331 after 30 minutes' sintering in argon at 1800°, 2000°, or 2200° F. All compacts have an admixture of 5 percent clay and were formed by slip casting. The stacked specimens were separated during sintering by alumina, which accounts for the bands of different appearance at the ends of some of the compacts.

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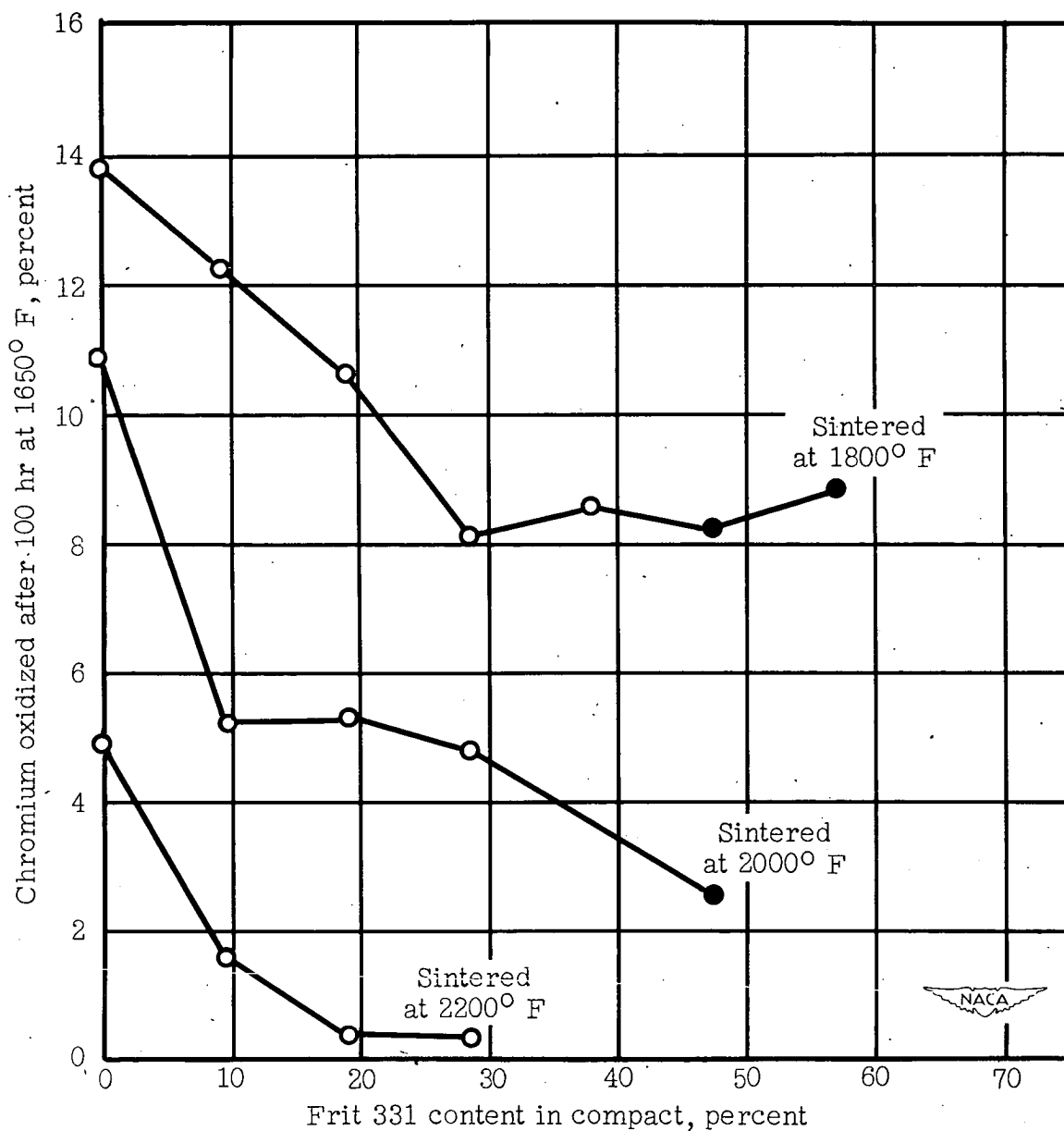


Figure 2.- Effect of frit 331 content and sintering temperature on the chromium oxidized after heating for 100 hours at 1650° F. Compacts represented by solid points were bloated after sintering and showed a honeycomb structure. All compacts were sintered in argon.

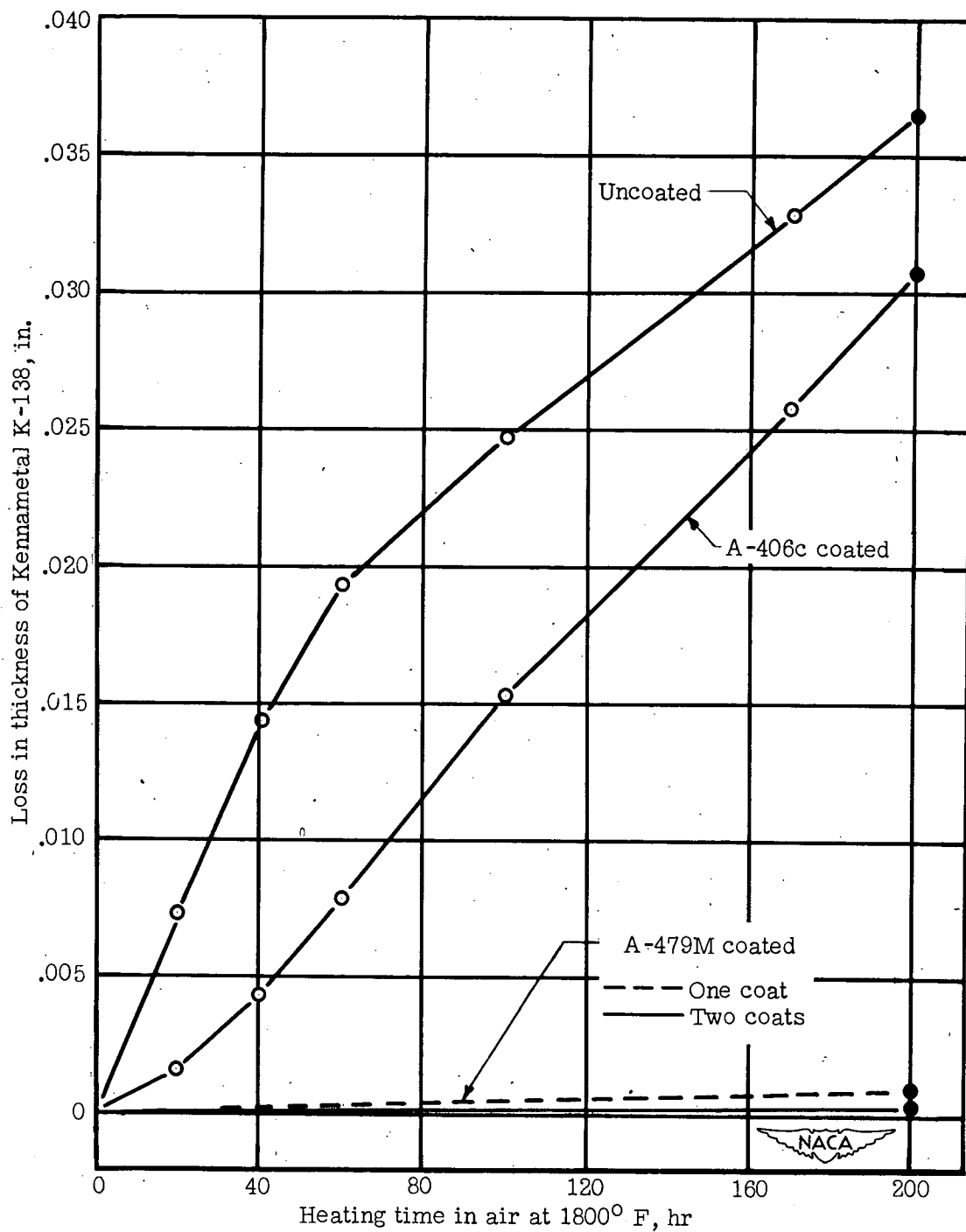
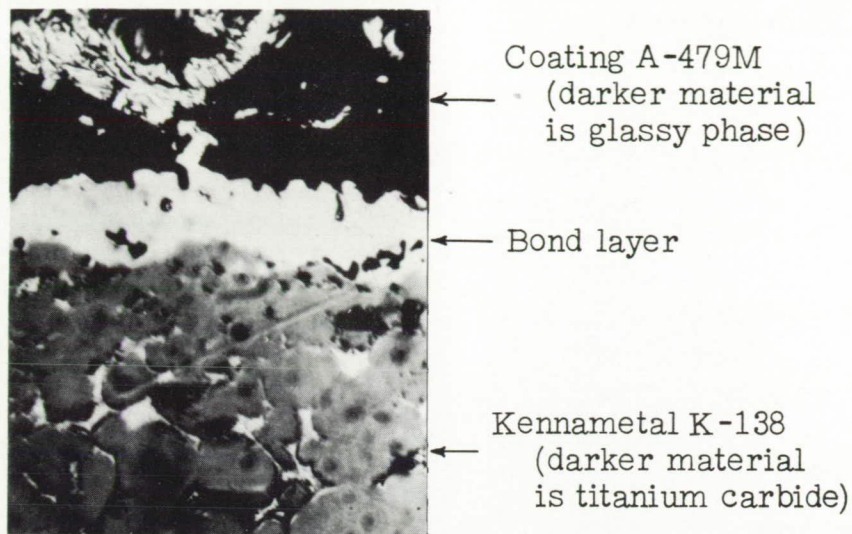
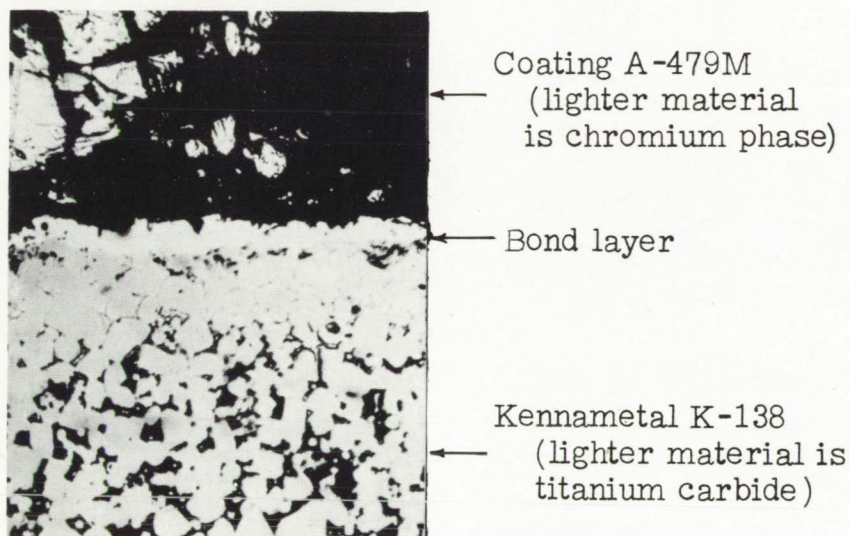


Figure 3.- Loss in thickness of both coated and uncoated specimens of Kennametal K-138 plotted against heating time in air at 1800° F. Solid points determined from micrometer measurements made before coatings were applied and again with coatings removed after 200 hours of heating. Other points calculated from gain in weight.



(a) Unetched section, X1750.



(b) Nital etched section, X800.



Figure 4.- Etched and unetched sections at two magnifications through coating-ceramic interface showing bond layer that forms when chromium-frit coating A-479M is applied to Kennametal K-138 and fired for 10 minutes at 2200° F in purified hydrogen. Note change in structure of K-138 as bond layer is approached.

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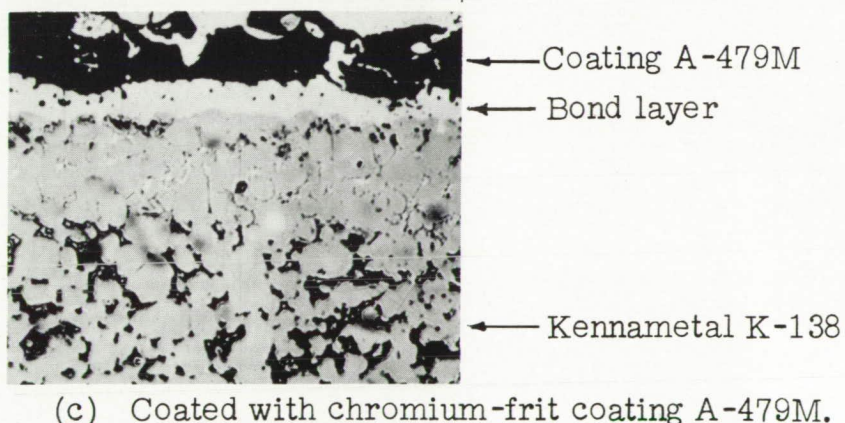
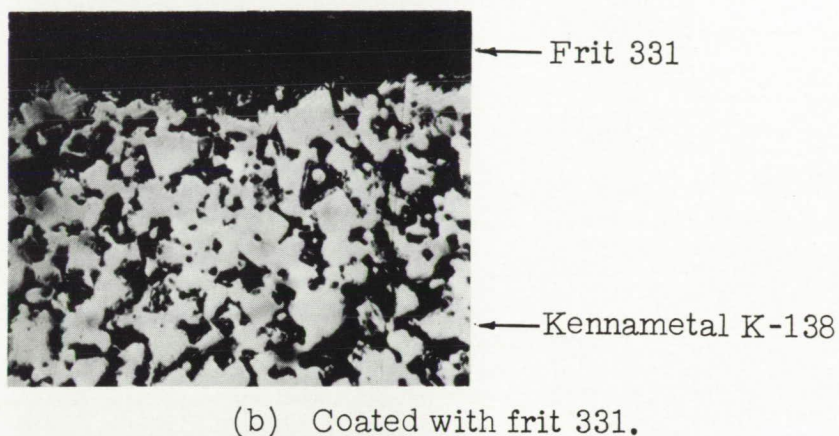
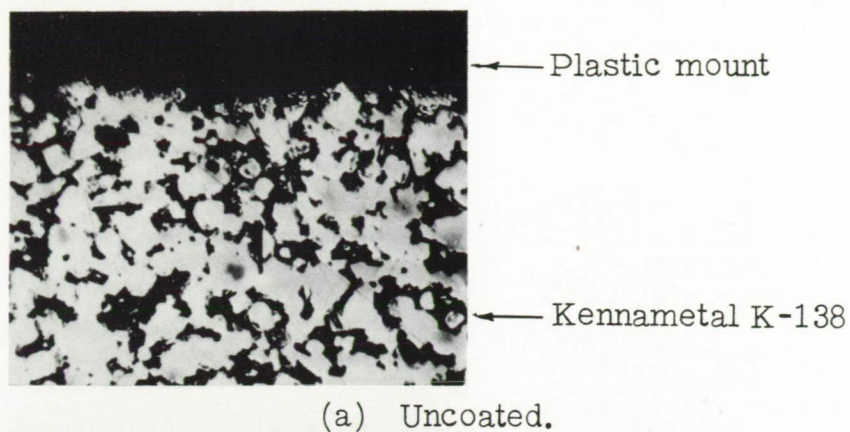
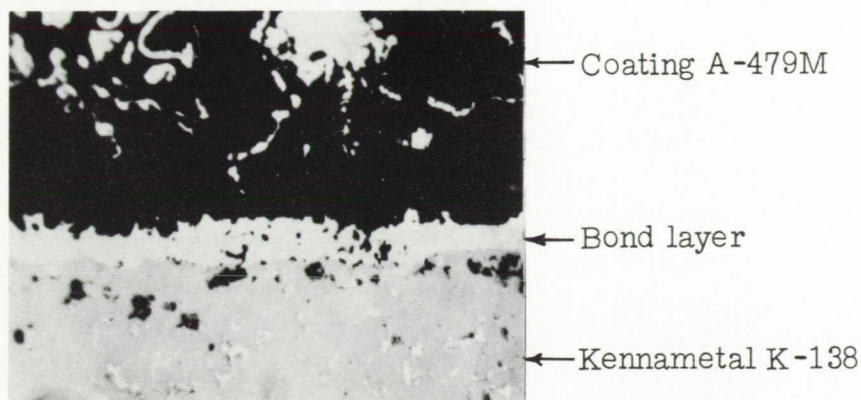


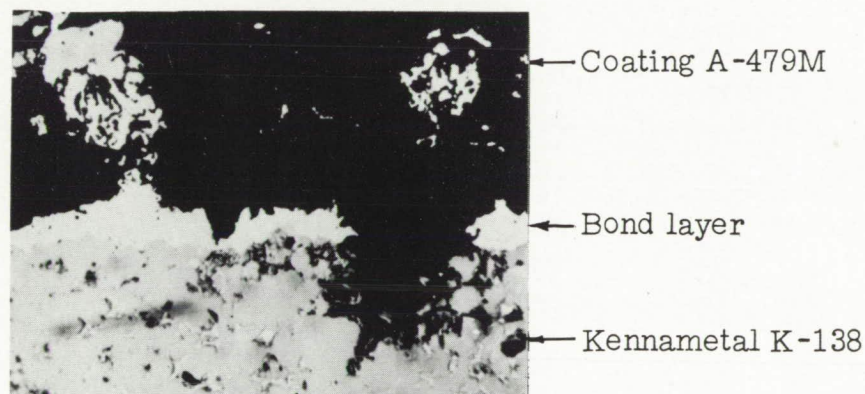
Figure 5.- Nital etched sections through coated and uncoated Kennametal K-138 specimens showing that development of the bond layer, as shown in figure 4, is dependent on presence of chromium. All specimens were fired in purified hydrogen for 10 minutes at 2200° F. The dark material in the coating is the glassy phase which is present as about 40 percent by volume, X1000.

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(a) Normal condition.



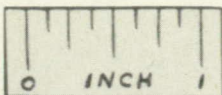
(b) Apparent oxidation of Kennametal K-138 attributed to localized break in coating.



Figure 6.- Unetched sections (X1000) across coating-ceramel interface after 200 hours' heating in air at 1800° F. Oxide penetration is approximately 0.001 inch at the oxidation pocket in (b) as compared with about 0.037-inch penetration for the uncoated Kennametal K-138 subjected to the same treatment.

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- (a) Compact pressed from coating A-483M and sintered in hydrogen for 30 minutes at 2200° F.



- (b) Same type of compact as above after testing with quarter-point loading at 2000 psi for 18 hours in air at 1500° F.

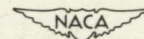


Figure 7.- Results of deformation test at 1500° F with compacts prepared from chromium-frit coating A-483M which is the same as A-479M except that it contains -200 mesh chromium rather than -100 mesh chromium. Measured deformation on tension side of lower specimen was 1.3 percent. No signs of cracking were observed in specimen after test.